

THE OPTICAL CONSTANTS OF LIQUID ALLOYS

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C. V. KENT

A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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SYNOPSIS.

This paper describes a determination of the two optical constants of molten metals, the index of refraction, ν , and the index of absorption, κ , from the reflection of polarized light at molten-metal surfaces, placed in an inactive atmosphere.

The *purpose* of this experiment is to throw some light upon the behaviour of free electrons in metals.

Method.—The constants, ν and κ , are computed from the phase change Δ , and the azimuth change ψ , of polarized light reflected from the surface of the liquid metal at an angle of incidence ϕ . A Jamin circle is employed, the azimuth of the analyzer being determined by a bi-field of new design.

A furnace for melting the metals is made up by winding a few yards of nichrome wire on a hollow iron cone, thus maintaining a temperature of about 400° C. The whole furnace is operated in a water-cooled container through which a stream of hydrogen is made to flow continuously.

The metals employed are bismuth, cadmium, tin, lead and binary alloys of these. As a source of light, three strong rays from a quartz mercury arc are used.

Results.—A good optical surface is obtained, free from the scratches and impurities of polishing materials.

Values of $\nu^2 - \kappa^2$ and $2\nu\kappa$, are plotted as functions of the composition (atomic concentration) of each alloy. The parameters of the free electrons are also computed and plotted as functions of the composition of the alloy. These parameters are: (1) the product Ne^2/m , where the symbols have the meanings usually given in the electron theory, and (2) the frequency of impact of a free electron with the molecules of the metal.

From these optically determined free electron parameters, the electrical resistivities of the pure liquid metals and alloys are computed. In every case the agreement with the known electrical resistivity is within the limits of experimental error. A possible explanation of the disagreement between the values of resistivities for solid metals as computed from optical data and from direct electrical measurement, is suggested.

The results seem to indicate that the simple free electron theory of Drude and others is applicable to molten metals.

I. INTRODUCTION.

THE optical constants of metals (*i.e.*, the indices of refraction and absorption) are of some importance in the free electron theory. They afford a fairly direct method of obtaining a knowledge of the approximate magnitudes of some of the free electron parameters. However, the values of these optical constants as obtained experimentally for metals in the solid state, are unexpectedly unsatisfactory and inconsistent.

This is due to several causes. It is obvious that the necessary experimental data are most readily obtained by determining the changes produced in light when it is reflected from the metal to be examined; these changes being of intensity and phase. The accuracy of results is thus limited by the photometrical sensibility of the eye.

Furthermore, it is almost impossible to obtain plane surfaces which are *optically* pure, by ordinary grinding and polishing. Scratches and traces of abrasive agents, imperceptible to the naked eye, produce surfaces quite different from those of the pure metal. Minor,¹ Erochin,² Duncan³ and others have minimized this source of error by using mirrors deposited on glass and examining the glass-metal inter-face. Their data show, however, that the optical constants vary with the method of producing the surfaces, whether by chemical processes, cathode deposition or casting. For these reasons, results obtained by different observers with the same metal, or even by the same observer with successive surfaces vary from 5 to 20 per cent.

The theoretical interpretation and correlation of data for different metals in the solid state is also open to objection. For example, the parameters controlling electron motion within the space lattice of a metallic crystal will be functions of direction of motion. It seems reasonable, therefore, to expect different values of the optical constants for different orientations. Thus, the optical constants of an extended solid metal surface are perhaps merely averages for the various crystals exposed.

In the course of an optical investigation of alloys, I decided to eliminate the above-named difficulties as far as possible, by restricting the work to liquid surfaces in an inactive atmosphere. By so doing, I could obtain surfaces which were perfectly smooth and practically free from contamination. Any small impurities would be either dissolved in the metal and be negligible in their effect, or, floating as solid aggregates, could be removed by mechanical means.

¹ R. S. Minor, Ann. d. Phys., 10, 581, 1893.

² P. Erochin, Ann. d. Phys., 39, 213, 1912.

³ R. W. and R. C. Duncan, Phys. Rev., 1, 294, 1913.

The investigation was further restricted to pure metals and bi-metallic alloys in which there were no compounds. In this simple case, the alloy may be considered from a theoretical point of view to consist of three mutually dissolved components: (1) The molecules of the first component metal and (2) of the second, each preserving the characteristics peculiar to the molecules of the pure metals, and (3) that portion to which metallic conduction is due. This portion is the free electrons common to all metals, and contributed in the case of the alloys here tested, by the two component metals.

II. PREVIOUS WORK.

A few determinations of the optical constants of alloys have been made, most of them for the various kinds of speculum metal. Bernouilli¹ has worked with the binary mixtures Ag-Te, Ag-Sn, Cd-Hg, Cu-Sn, Cu-Zn and Cu-Ni; in each case, only a small portion of the latter component was present. Littleton² investigated the effect of the carbon content in various steels, and in another paper has taken up the systematic study of iron-nickel, nickel-silicon, iron-manganese, aluminum-copper, copper-nickel and iron-copper alloys. His efforts were chiefly directed to tracing the effects of the presence of compounds of the components present. Recently L. K. Oppittz³ has studied the binary alloys of silver with copper and platinum.

Practically no results have been obtained for liquid metals with the exception of mercury. Drude mentions his apparently unsuccessful attempts to work with melted tin; he also gives some values of the optical indices for mercury alloyed with 2 per cent. tin, and for liquid Wood's metal. No other data for liquid metals has been found.

III. METHOD.

This is the familiar method employed in the investigation of opaque substances. Light incident upon the reflecting surface to be examined, is plane polarized in a plane at an angle of 45 degrees to the plane of incidence. The difference of phase between the two components of the reflected light is determined by a phase compensator which again plane polarizes the light passing through it. The azimuth of the plane of polarization of this light is determined by an analyzer.

Let the angle of incidence be ϕ , the phase difference introduced by reflection be Δ , and the azimuth of the plane of polarization of the reflected light with respect to the plane of incidence be ψ . In conformity

¹ A. Bernouilli, *Zeitschr. f. Elektrochemie*, 15, 647, 1909.

² J. T. Littleton, *PHYS. REV.*, 28, 306, 1912; 33, 453, 1912.

³ L. K. Oppittz, *PHYS. REV.*, 10, 156, 1917.

with the terminology of many investigators in this subject, I have adopted the optical constants ν and κ , which are equal to Drude's n and nk respectively. The following convenient reduction formulæ may then be used to calculate ν and κ .

$$\cos 2P = \sin 2\psi \cos \Delta, \quad \tan Q = \tan 2\psi \sin \Delta,$$

$$S = \sin \phi \tan \phi \tan P,$$

$$\nu^2 - \kappa^2 = S^2 \cos 2Q + \sin^2 \phi = A,$$

$$2\nu\kappa = S^2 \sin 2Q = B.$$

Hence

$$2\nu^2 = \sqrt{A^2 + B^2} + A,$$

$$2\kappa^2 = \sqrt{A^2 + B^2} - A,$$

ν , κ , and the reflecting power at perpendicular incidence may then be found.

IV. DESCRIPTION OF APPARATUS.

Monochromatic Illuminator.—A Cooper-Hewitt quartz tube mercury arc was used as a source of illumination. Its light was separated into its component colors by a Wadsworth prism-mirror train. The three intense lines, 404 $\mu\mu$, 546 $\mu\mu$ and 578 $\mu\mu$ (violet, green and yellow) were used. The colored slit image of the slit in the Wadsworth train covered the collimator slit, the collimator lens being completely filled at all times with the light employed.

Spectroscope and Polarization Train.—The spectroscope was a "Cercle de Jamin" from the Société Genevoise and is evidently intended for this sort of work. As liquid surfaces were used the circle was turned into a vertical plane. The verniers of the telescope and collimator gave their position on the spectroscope circle to 30".

The polarizer and analyzer were mounted on the objective lens end of the collimator and telescope respectively. The nicols were of the Glan-Thompson type with about 1 cm. aperture. They were perfect in action. Their divided circles could be read by verniers to 6'.

The compensator was mounted between the polarizer and the reflecting surface. It was of the Soleil-Babinet type; the micrometer head of the screw moving the quartz wedge was divided into 100 parts, each corresponding roughly to about 1/2 degree. Thus by estimating to tenths of a division, an accuracy of about 3' could be obtained.

The writer's experience with this compensator is identical with that of R. W. and R. G. Duncan, in that it is impossible to obtain uniform darkness over the whole field of view. With the compensator and analy-

zer adjusted for minimum illumination, if the telescope eyepiece was removed, the field of view presented a blotched or striated appearance. With the eyepiece in place, the collimator slit image was traversed by a dark and fairly narrow diagonal band, which shifted position very rapidly with slight changes in the compensator setting. It is probable that this defect in the action of the compensator is due to some irregularity of crystal structure in the quartz plates.

In order to use the compensator for its purpose the practice was adopted of taking all compensator readings when the center of the black band lay under the intersection of the telescope crosshairs. This was done both in the preliminary calibration of the compensator, *i.e.*, in the determination of the phase shift per division on the compensator micrometer head for each color of light used, and in the regular experimental work. In this latter work, what was measured was the phase shift necessary to bring the diagonal band back under the cross hairs when it was shifted by reflection. From the results of a number of preliminary experiments the writer is convinced that no errors were introduced by this method of using the compensator.

Bi-field.—Total extinction of the light after it was reflected could never be produced in this experimental work by any adjustments of compensator and analyzer. This was due to the following causes: the imperfection of the compensator described above; films of moisture or metal on the observation windows of the housing of the heater in which the metal was melted; sources of scattered light such as dust particles, etc., in the optical train between the nicol prisms. An azimuth bi-field was therefore absolutely necessary for determining the azimuth position of the analyzer.

An entirely new form of bi-field was invented by the writer for this purpose in 1913. It was subsequently described by Dr. F. E. Wright,¹ of the Geophysical Laboratory. As the mounting and use by the writer is quite different from the adaptation of Dr. Wright, a brief description will be given.

The bi-field (see Fig. 1) consists of two slips of glass mounted on, and rotating with the analyzer. They are situated, of course, in the beam of light from the polarizer to the analyzer. Satisfactory slips are easily cut from a good strain-free microscope slide. The slips abut along a common edge and are inclined to each other at a somewhat obtuse angle, perhaps 120 degrees. Their common edge is in (or perpendicular to) the plane of polarization of the analyzer and their faces make equal angles with the direction of the beam of light passing through them and the

¹ F. E. Wright, Wash. J. Sci., 4, 309, 1914.

analyzer. The common edge is also inclined at an angle with the direction of the beam of light; the inclination is variable in order to change the sensibility of the bi-field.

When the bi-field is in use, a short focus telescope is substituted for the eyepiece of the spectroscope telescope and focused upon the common edge of the glass slips.

The field of view is thus divided in halves by this edge. The "crossed" or extinction position of the analyzer is denoted by equality of brightness of the halves of the field. The arrangement acts exactly as the usual quartz bi-field of variable sensitivity.

The dividing line between the halves of the field is practically eliminated (1) by mounting the glass slips with the exterior obtuse angle toward the incoming beam of light, and (2) by grinding the adjacent edges of the slips or plates to a rough fit. The interior edge of one plate is finished very sharply and overlaps the other. Thus this finely finished edge serves as a common dividing line and is practically invisible.

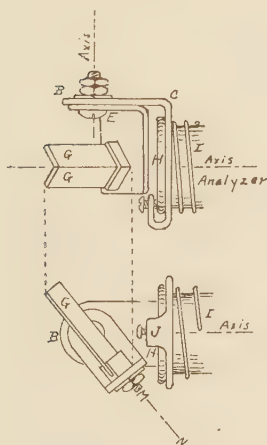


Fig. 1.

Multiply reflected light is present in the field of view except in a narrow band on each side of the dividing line. As the sensitivity is much reduced by this multiply reflected light, only the narrow bands are observed when obtaining the position of equal brightness.

In order to properly adjust the bi-field to the position described above it is mounted as shown in the accompanying figure. (Fig. 1).

The theory of its action is simple. Consider plane-polarized light incident upon one of the glass plates and resolve it into its two components in, and perpendicular to, the plane of incidence. By transmission these are unequally diminished with no phase difference introduced, according to the ordinary Fresnel laws. After transmission these again combine to form light of slightly diminished intensity, and on account of the inequality of diminution, plane-polarized in a slightly different plane from that of the incident light. In other words the light has been slightly diminished in intensity and *rotated through a small angle*. The light passing through the other plate will be likewise decreased in intensity and its plane of polarization also rotated, but in the opposite direction. If, now, the analyzer is in the "crossed" or total extinction position, the two glass plates are symmetrically situated, both with respect to the analyzer and the plane of polarization of the incident light.

In this case the lights passing through the two plates are equal in brightness and their planes of polarization equally rotated, but in opposite directions, with respect to the plane of polarization of the analyzing nicol. Therefore when they are observed through the analyzer the two halves of the field will be of equal brightness. When the analyzer (and glass plates) are in any other position, equality of brightness will not obtain.

The action of this bi-field is the same when it is mounted on the polarizer instead of the analyzer, and in the same position with respect to the plane of polarization of this nicol. The common edge may also be in a plane perpendicular to the plane of polarization of the nicol on which it is fastened. Owing to the mounting used, all adjustments of the bi-field for its proper action can be made optically by simple methods which need not be described here. The angle between the planes of polarization of the beams of light passing through the two plates, can be varied from 0 to about 12 degrees.

The arrangement described seems to have all the advantages of the quartz bi-field of variable sensibility. In addition its cost is insignificant and it is very easily constructed.

V. FURNACE AND CONTAINER.

These were mounted on a heavy laboratory tripod beside the spectro-scope circle. They could be easily swung out from between the collimator and telescope at any time for adjustment, etc.

The necessary details of the heater and container for the hydrogen atmosphere above the liquid metal may be seen from the accompanying diagram (Fig. 2).

The heater, *Q*, consisted of about 8 m. of no. 28 nichrome wire imbedded in an asbestos water-glass cement. The liquid metal was held in the iron cone *Q*, whose surface was rubbed with steatite to prevent adherence. *S* is a protecting asbestos rim; an overhanging roof protects the binding posts *R*, from spilled metal. Wires from the heating coil are led outside the container through the tube *D*, in the base. The asbestos bottom of the heater is cut away over the exit tube *E* to allow for egress of detritus and samples of the metal used.

The container was made in two parts, both water-cooled. When in use these were cemented together by soft wax. The base of the container consisted of a sheet metal cylinder 12 cm. in diameter and 2 cm. high. The tubes *A* and *B* in this, are for the ingress and egress of water, *D* for the heater wires, and *E* for the dumping of detritus and samples into a beaker of water below, into which it projected. Hydrogen, which flowed slowly through the apparatus during observations, bubbled out through this tube.

The upper portion of the container was made of two concentric sheet iron cylinders soldered together at the bottom edge. The space between these was utilized for cooling water, the outer cylinder being open at the top. *F* and *G* are two short tubes to which the observation windows (two strain-free microscope slides) were fastened with soft wax. Light to and from the reflecting liquid metal surface passed through these plates practically perpendicularly. Deviations of a degree or so from this perpendicularity were found to produce no change in the analyzer settings.

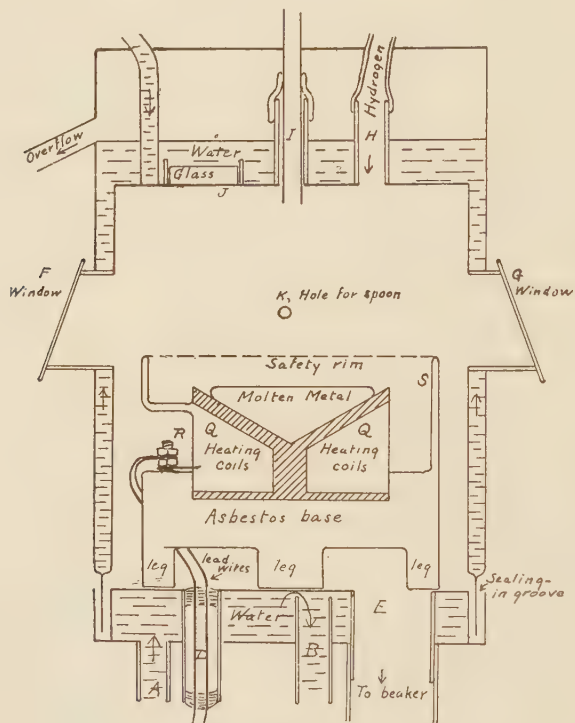


Fig. 2.

Tube *H* at the top of the container, was connected with a Kipp hydrogen generator. A glass tube slipped through tube *I*, the sliding joint being rendered gas tight by a gum rubber collar. This tube was used for the introduction of new metal when changing the composition of the alloy under observation. For this purpose it was pushed down until the lower end was immersed beneath the surface of the liquid metal. The component metal to be added was poured down through it in granular form, the tube corked and lifted up to its former position. Thus the interior of the container was at no time open to the air. *J* is an additional

glass window, for the general illumination of the interior of the container, if it should be needed.

At *K*, the sides of the inner and outer container walls were pressed together and soldered, and a small hole bored through both. A short brass collar was soldered over the hole on the outside. Over this was fastened a rubber finger stall. The handle of the "skimming spoon" (to be described later) was passed through this hole into the finger stall and could be manipulated from the outside.

It was impossible to obtain a clear liquid surface when the metal was first introduced into the heater and melted. The surface was therefore freed from oxide and other coarse impurities originally present by skimming with a specially formed spoon, whose handle projected into the finger stall on the outside, as previously described. The bowl of the spoon was a sheet iron cone of practically the same shape and dimensions as the cone in which the metal was melted. A hole 1 mm. in diameter was bored at the bottom point of this cone. The stiff wire handle which passed through *K* was covered with a short piece of clay pipe stem within the finger stall. The spoon was freely movable from outside, over, and in the molten metal. It was used much like the old fashioned cream skimmer; when it was dipped into the metal and raised, the clean metal ran back through the hole, leaving the gross impurities in the spoon; these were then dumped down the exit tube *E*.

VI. PRELIMINARY ADJUSTMENT OF THE OPTICAL SYSTEM.

The ordinary adjustments of the spectroscope need no description. It should be stated, however, that as the horizontal plane of the liquid reflecting surface was fixed, the optic axis of the spectroscope circle had to be brought into coincidence with it, by means of the leveling screws on the base of the instrument.

Orientation of the Plane of the Polarizer.—The ordinary means of finding this by means of reflection from a plane glass surface was found to be too inaccurate. A method was therefore devised which was quite satisfactory and is believed to be new. The compensator was removed from the instrument and the light from the polarizer, reflected from a clean pool of mercury (or other good metal surface), was examined by the analyzer. Both nicols were rotated alternately until total extinction was secured. In this case, the light coming from the metal mirror to the analyzer must have been plane polarized. Metal surfaces, however, always produce a difference of phase between the components of the reflected light in, and perpendicular to, the plane of polarization. It is evident therefore that one of these must have been absent in the reflected

and also the incident light. It is therefore also evident that the planes of polarization of the two nicols must likewise be in and perpendicular respectively to the plane of incidence of the light. In which of the two planes the light from the polarizer is polarized, can be easily determined if necessary by various simple methods which need not be discussed here.

Successive positions of the polarizer as obtained by this method always agreed within the least count of the polarizer circle, *i.e.*, 6'.

The zero phase difference readings of the compensator were found to be very slightly different for the three colors used. This instrument was also found to possess a small temperature coefficient which was negligible, however, in comparison with other sources of error.

Adjustment of Bi-Field.—This is entirely optical. With the compensator removed, the analyzer and polarizer were "crossed." The common edge of the bi-plate was set approximately perpendicular to the axis of the beam of light and the bi-plane turned until its faces made *unequal* angles with the beam. The whole bi-plate mounting was then rotated on the cap of the nicol holder until total extinction of the beam was produced *through* the plates. It should be stated, that for this work the short focus telescope previously mentioned, was used as eyepiece. The common edge now lay in the plane of polarization of the analyzer, and the mounting was therefore clamped to the cap. Next, the common edge being inclined 10° to 20° to the direction of the beam of light, the bi-plate was rotated around this edge until the intensity of the halves of the field was the same. The plates now made equal angles with the beam of light, and the bi-plate bolt was clamped to the arm on which it was supported.

VII. EXPERIMENTAL PROCEDURE AND CALCULATIONS.

Preparing the Surface.—After the metal had been placed in the heater and the container sealed over it, hydrogen was run through the apparatus gently for about half an hour to wash out the air. The circulation of the cooling water was then started and the furnace current turned on. As no change of the optical constants of the metals with temperature could be detected, the temperature was merely kept well above the melting point, at about 400° C.

After the first fusion, the metal was cleared of dross with the skimming spoon. Traces of oxygen from the surrounding atmosphere or surfaces in the container, seemed to act on the newly skimmed surfaces until completely exhausted. When the surface was quite clean it became extremely mobile with minute pieces of oxide floating here and there. At this stage the container was swung into place beside the spectroscope

circle and raised to the proper height, and the compensator and analyzer were roughly adjusted for minimum intensity of illumination. The surface was then examined without the telescope eyepiece. Surface impurities showed prominently as bright flecks or long streaks and were removed as far as possible by skimming. Those ultimately remaining usually travelled to the convex edge of the liquid as previously noted by Bidwell with similar surfaces. At the higher temperatures, actual reduction of the final oxide particles seemed to take place.

Readings.—These usually agreed within the limits of experimental error when made upon freshly cleaned surfaces. The surfaces of many alloys showed a progressive decrease of phase when left standing, although the analyzer readings were practically unaffected. It was therefore desirable to take the readings as rapidly as possible and the following order of taking observations was accordingly adopted:

1. The polarizer was set with its plane of polarization at 45° with the plane of incidence. Using the short focus telescope and bi-field, the analyzer was then accurately "crossed" with the reflected beam of light. Using the regular telescope eyepiece, the compensator was adjusted until the dark band in the slit image lay under the telescope cross hairs. Ten such compensator readings were taken for each of the three colors used.

2. The polarizer was turned through 90° and the compensator readings of 1 above repeated.

3. Using the bi-field and the short focus telescope as an eyepiece, five readings of the analyzer for a photometrically balanced field, for each of the three colors used, were taken.

4. The polarizer was turned back through 90° and 3 repeated.

5. 1 was repeated with yellow light to test possible change in the surface.

Owing to the perfection of the nicols and their divided circles it was found to be unnecessary to turn either polarizer or analyzer to positions approximately 180° from those already used. For positions of the polarizer 90° apart, the mean compensator readings were found to be consistently different by an amount varying from a few tenths to about 1° of phase difference. The cause of this consistent difference is unknown, but undoubtedly lies in the imperfections of the compensator.

Calculation of Optical Constants.—Mean values were taken in all calculations. The determinations of the angle of incidence and the phase difference indicated by the compensator are sufficiently obvious. The difference between the two mean analyzer positions for the two polarizer azimuths of 3 and 4 above was taken as 2ψ . It may have been the complement of 2ψ but as the substitution of this complement in the

reduction formula used to calculate the optical constants merely produced a change of sign in the values of these constants, this uncertainty gave no trouble. For metals, $\nu^2 - \kappa^2$ is always negative, and $2\nu\kappa$ positive. The reflecting power at perpendicular incidence was calculated from the formula¹

$$R = \frac{\nu^2 + \kappa^2 + 1 - 2\nu}{\nu^2 + \kappa^2 + 1 + 2\nu}.$$

VIII. RESULTS.

The alloys used were bismuth-lead, cadmium-lead, tin-lead and bismuth-mercury. The metals were obtained from the chemical laboratory and were pure.

1. *Bismuth-lead*.—These were very satisfactory from an optical standpoint. After skimming well, the alloy surfaces remained clean indefinitely, as the hydrogen atmosphere seemed to reduce any oxide flecks remaining.

2. *Cadmium-lead*.—The cadmium evaporated quite freely from these alloys and formed bright mirrors on the observation windows in the course of an hour or so. The depolarizing effect of the films made the compensator band faint and hazy and gave the field of the bi-plate a mottled appearance, but very good readings could be taken when the mirrors were so opaque that no details of the alloy surfaces could be seen.

3. *Tin-lead*.—Work with these alloys was extremely difficult. A few seconds after the formation of a new and clean surface, fine lines of what seemed to be minute bubbles appeared and spread until the whole surface was covered with a viscous scum, probably oxide. This formation was never entirely prevented, even when the atmosphere was practically pure hydrogen. It is probably due to oxygen originally in solution in the tin. On this account, the surface of the pure tin (or of alloys rich in this component) was renewed after every two or three readings. These readings were reproducible and the phase difference indicated by the compensator was a maximum.

4. *Bismuth-mercury*.—The accuracy of results with these alloys is relatively poor. This is due to the condensation of mercury on the observation windows, and the low temperatures necessarily employed, which prevented any reducing effect by the hydrogen.

Composition of the Alloys.—As an accuracy of more than one per cent. was not necessary, simple gravimetric determinations of the composition were made. The samples obtained from each alloy were dissolved in nitric acid. Lead was estimated as sulphate in each case, bismuth as tetroxide, cadmium as nitrate, and tin as oxide. No chemical analysis

¹ Houston, A Treatise on Light, p. 417.

of the bismuth-mercury alloy was made. In the following tables the alloys will be defined by the atomic per cent. of one component.

Tables.—The experimentally determined values of the angle of incidence ϕ , twice the azimuth angle of the reflected light (2ψ), and the phase difference, Δ , are given for each of the alloys examined. From these are calculated the optical constants $\nu^2 - \kappa^2$, $2\nu\kappa$, ν , κ and R the reflecting power at perpendicular incidence.

TABLE I.
Bismuth-lead Alloys.

Alloy.		ϕ .	2ψ .	Δ .	$\frac{\nu^2 - \kappa^2}{2\nu\kappa}$	$2\nu\kappa$.	ν .	κ .	Refl. Power, Per Cent.
579 μ .									
Bismuth (pure)	A	70° 32'	63° 47'	125° 48'	9.64	20.27			
	A	70° 36'	63° 37'	124° 41'	9.36	19.47			
	B	70° 35'	64° 3'	124° 41'	9.77	19.72			
Mean values					9.62	19.72	2.48	3.97	64.4
6 per cent. lead.	C	70° 35'	64° 36'	126° 9'	10.52	20.53			
	D	70° 35'	63° 58'	124° 38'	9.69	19.40			
Mean values					10.10	19.97	2.52	4.00	64.5
19 per cent. lead.	E	70° 33'	64° 6'	124° 44'	9.79	19.37			
	F	70° 33'	64° 30'	126° 50'	10.51	21.06			
Mean values					10.15	20.21	2.48	4.03	65.0
26.4 per cent. lead	I	70° 33'	65° 11'	126° 23'	11.08	20.52	2.57	4.09	65.2
48 per cent. lead.	J	70° 33'	65° 16'	126° 14'	11.64	21.24			
	K	70° 33'	65° 36'	127° 17'	11.67	21.22			
Mean values					11.66	21.23	2.56	4.20	65.7
60 per cent. lead.	M	70° 33'	66° 14'	127° 1'	12.24	20.85			
	N	70° 33'	65° 54'	128° 17'	12.19	22.10			
Mean values					12.22	21.47	2.55	4.26	66.8
75 per cent. lead.	O	70° 33'	67° 28'	128° 48'	14.03	22.17			
	P	70° 33'	67° 12'	128° 14'	13.58	21.70			
Mean values					13.81	21.94	2.62	4.37	67.4
86 per cent. lead.	Q	70° 33'	67° 23'	128° 53'	13.96	22.26	2.50	4.48	69.0
Lead (pure).	R	70° 37'	67° 46'	129° 17'	14.63	22.74			
	S	70° 36'	68° 10'	129° 17'	15.04	22.48			
Mean values					14.84	22.61	2.56	4.53	69.2

Alloy.		ϕ .	2ψ .	Δ .	$\left(\frac{2\psi}{\phi}\right)$.	$2\nu_K$.	ν .	κ .	Ref. Power Per Cent.
546 μ .									
Bismuth (pure)	A	70° 32'	63° 53'	123° 36'	9.39	18.51.			
	A	70° 36'	63° 47'	123° 14'	9.25	18.26			
	B	70° 35'	63° 43'	121° 56'	8.96	17.34			
Mean values					9.20	18.04	2.35	3.84	63.8
6 per cent. lead	C	70° 35'	64° 3'	123° 41'	9.54	18.53			
	D	70° 35'	64° 4'	122° 46'	9.39	17.87			
Mean values					9.47	18.20	2.35	3.87	64.1
19 per cent. lead	E	70° 33'	64° 2'	123° 8'	9.42	18.13	2.35	3.86	64.1
26.4 per cent. lead . .	H	70° 33'	65°	125° 58'	10.80	20.17			
	I	70° 33'	65° 9'	125° 46'	10.90	19.97			
Mean values					10.85	20.07	2.44	4.10	65.9
48 per cent. lead	J	70° 33'	65° 26'	124° 4'	10.78	18.54			
	K	70° 33'	65° 42'	122° 2'	10.51	16.94			
Mean values					10.65	17.74	2.24	3.96	65.2
61 per cent. lead	L	70° 33'	66° 28'	124° 14'	11.69	18.36			
	M	70° 33'	66° 25'	126° 6'	12.13	19.97			
	N	70° 33'	66° 12'	126° 24'	12.05	20.25			
Mean values					11.96	19.53	2.34	4.18	67.3
75 per cent. lead	O	70° 33'	67° 29'	126° 24'	13.30	19.94			
	P	70° 33'	66° 56'	126° 0'	12.66	19.73			
Mean values					12.98	19.84	2.32	4.28	68.4
86 per cent. lead	Q	70° 33'	67° 40'	127° 0'	13.65	20.33	2.33	4.37	66.1
Lead (pure)	R	70° 36'	68° 18'	127° 29'	14.57	20.71			
	S	70° 37'	68° 18'	127° 23'	14.56	20.65			
Mean values					14.56	20.68	2.42	4.46	69.5
404 μ .									
Bi	A	70° 32'	63° 43'	111° 48'	7.06	11.80	1.80	3.23	60.6
Pure									
6 per cent. lead	D	70° 35'	62° 50'	110° 54'	6.62	11.66	1.85	3.15	69.0
18 per cent. lead	E	70° 33'	63° 49'	111° 54'	7.09	11.77	1.82	3.23	60.3
26.4 per cent. lead . .	I	70° 33'	65° 24'	111° 54'	7.85	11.40	1.73	3.29	62.1
48 per cent. lead	J	70° 33'	66° 1'	112° 21'	8.31	11.52			
	K	70° 33'	66° 13'	113° 54'	8.79	12.15			
Mean values					8.55	11.84	1.74	3.40	63.5

Alloy.		ϕ .	2ψ .	Δ .	$\left(\frac{n_D}{n_F} - \frac{n_D}{n_C}\right)$	$2\nu_K$.	ν .	κ .	Refl. Power, Per Cent.
579 μ m.									
61 per cent. lead....	L	70° 33'	66° 56'	112° 36'	8.83	11.33			
	M	70° 33'	66° 41'	114° 6'	9.08	12.11			
	N	70° 33'	65° 32'	114° 30'	8.57	12.61			
Mean values.....					8.83	12.02	1.74	3.45	64.0
75 per cent. lead....	O	70° 33'	65° 32'	115° 18'	8.77	13.02			
	P	70° 33'	67° 40'	114° 48'	9.78	12.15			
Mean values.....					9.28	12.59	1.78	3.53	64.6
86 per cent. lead....	Q	70° 33'	68° 30'	115° 6'	10.30	12.01	1.66	3.61	67.0
Pure lead.....	R	70° 36'	69° 6'	116° 18'	11.11	12.48			
	S	70° 37'	69° 54'	115° 34'	11.23	11.74			
Mean values.....					11.17	12.11	1.63	3.72	68.5

TABLE II.
Cadmium-lead Alloys.

Alloy.		ϕ .	2ψ .	Δ .	$\left(\frac{n_D}{n_F} - \frac{n_D}{n_C}\right)$	$2\nu_K$.	ν .	κ .	Refl. Power, Per Cent.
579 μ m.									
Cadmium (pure) ...	A	70° 37'	82° 38'	126° 36'	25.66	8.78			
	B	70° 37'	83° 56'	127° 0'	26.74	7.49			
	C	70° 37'	82° 8'	127° 6'	25.99	9.61			
	D	70° 37'	82° 56'	126° 0'	25.19	8.19			
Mean values.....					25.72	8.15	0.82	5.14	89.8
12 per cent. lead....	F	70° 37'	81° 22'	126° 42'	25.14	10.23	1.00	5.11	86.7
22 per cent. lead....	H	70° 36'	77° 23'	127° 42'	23.30	14.88			
	I	70° 36'	77° 54'	127° 0'	23.06	13.86			
Mean values.....					23.19	14.37	1.43	5.02	81.6
33.5 per cent. lead..	J	70° 36'	75° 43'	128° 24'	22.46	16.96	1.69	5.03	79.3
52.5 per cent. lead..	K	70° 36'	73° 53'	128° 12'	20.56	18.24	1.86	4.90	76.2
64 per cent. lead....	L	70° 36'	72° 26'	127° 30'	18.98	19.03	1.99	4.79	75.0
76 per cent. lead....	M	70° 36'	69° 58'	127° 54'	16.44	20.36	2.21	4.62	72.0
79.5 per cent. lead..	N	70° 36'	69° 40'	128° 15'	15.59	20.00	2.21	4.53	71.2
Pure lead.....					14.84	22.61	2.56	4.53	69.2

Alloy.		ϕ .	2ψ .	Δ .	$\frac{\alpha_2}{\alpha_1}$ $\left(\frac{\mu_2}{\mu_1}\right)$	$2\eta_K$.	ν .	κ .	Ref. Power, Per Cent.
546 $\mu\mu$.									
Cadmium (pure)....	A	70° 37'	82° 18'	123° 24'	22.32	7.32			
	B	70° 37'	83° 56'	124° 0'	23.52	6.33			
	C	70° 37'	82° 11'	124° 10'	22.81	8.07			
	D	70° 37'	82° 40'	124° 12'	23.20	7.68			
Mean values.					23.16	7.45	0.76	4.87	88.6
12 per cent. lead....	F	70° 37'	81° 24'	123° 36'	22.09	8.64	0.90	4.79	86.4
22 per cent. lead....	H	70° 36'	77° 18'	125° 16'	21.14	13.16			
	I	70° 36'	77° 54'	125° 40'	21.02	12.57			
Mean values.					21.08	12.87	1.14	4.78	83.4
33.5 per cent. lead..	J	70° 36'	75° 48'	126° 36'	21.07	15.38	1.58	4.86	79.0
52.5 per cent. lead..	K	70° 36'	74° 4'	126° 4'	19.25	16.25	1.72	4.71	76.7
64 per cent. lead....	L	70° 36'	72° 13'	125° 17'	16.17	17.11	1.92	4.46	72.2
76 per cent. lead....	M	70° 36'	70° 10'	125° 37'	15.52	18.14	2.04	4.44	71.1
79.5 per cent.	N	70° 36'	70° 4'	125° 29'	15.38	18.10	2.05	4.42	71.6
Pure lead.					14.56	20.68	2.42	4.46	69.5
404 $\mu\mu$.									
Cadmium (pure)....	A	70° 37'	82° 12'	109° 6'	12.62	4.00			
	B	70° 37'	85° 23'	107° 18'	12.16	2.22			
	C	70° 37'	82° 11'	109° 27'	12.79	4.07			
Mean values.					12.52	2.76	0.39	3.56	93.1
12 per cent. lead. ...	E	70° 37'	82° 25'	108° 6'	12.17	3.73			
	F	70° 37'	82° 12'	109° 54'	13.01	4.14			
Mean values.					12.59	3.94	0.55	3.59	85.6
22 per cent. lead....	H	70° 36'	78° 28'	111° 48'	13.11	6.37			
	I	70° 36'	80° 0'	112° 6'	13.63	5.73			
Mean values.					13.37	6.05	0.81	3.74	81.4
33.5 per cent. lead..	J	70° 36'	77° 0'	113° 42'	13.57	7.78	1.02	3.82	78.2
52.5 per cent. lead..	K	70° 36'	75° 5'	113° 15'	12.65	8.58	1.15	3.74	75.2
64 per cent. lead....	L	70° 36'	73° 10'	112° 54'	11.74	9.30	1.27	3.66	72.4
76 per cent. lead....	M	70° 36'	70° 40'	113° 6'	9.56	10.47	1.52	3.45	66.6
79.5 per cent. lead..	N	70° 36'	70° 2'	113° 48'	10.71	10.94	1.52	3.61	68.6
Pure lead.					11.17	12.11	1.63	3.72	68.5

TABLE III.

Tin-lead Alloys.

Alloy.		ϕ_*	$2\psi_*$	Δ_*	$\left(\frac{1}{\rho}\right)_*$	$2\mu\kappa_*$	ν_*	κ_*	Refl. Power, Per Cent.
579 $\mu\mu$.									
Tin, pure	A	70° 33'	76° 38'	131° 40'	26.24	19.21			
	H	70° 41'	76° 55'	131° 54'	27.24	19.47			
Mean values					26.74	19.34	1.77	5.47	81.1
7 per cent. lead.	I	70° 41'	77° 22'	131° 3'	24.68	20.12	1.89	5.32	79.3
21 per cent. lead.	B	70° 33'	75° 40'	131° 48'	25.28	20.32	1.89	5.37	79.7
37.5 per cent. lead.	C	70° 33'	73° 38'	130° 30'	21.83	20.62	2.03	5.09	76.9
62 per cent. lead.	D	70° 33'	71° 18'	129° 37'	18.67	21.28	2.20	4.85	73.9
85.5 per cent. lead.	E	70° 36'	70° 47'	129° 30'	17.86	21.46	2.24	4.78	73.1
Pure lead.					14.84	22.61	2.56	4.53	69.2
546 $\mu\mu$.									
Tin, pure	A	70° 33'	76° 4'	131° 27'	25.38	19.53			
	H	70° 41'	77° 13'	130° 7'	25.68	17.32			
Mean values					25.53	18.43	1.73	5.34	80.8
7 per cent. lead.	I	70° 41'	76° 22'	129° 11'	24.00	17.27	1.70	5.18	80.3
21 per cent. lead.	B	70° 33'	74° 47'	127° 53'	22.15	18.48	1.83	5.05	78.1
37.5 per cent. lead.	C	70° 33'	73° 10'	127° 53'	19.54	18.36	1.91	4.81	75.9
62 per cent. lead.	D	70° 33'	71° 18'	127° 20'	17.17	18.78	2.04	4.62	73.3
85.5 per cent. lead.	E	70° 36'	71° 24'	126° 36'	17.20	18.40	2.00	4.60	73.5
Pure lead.					14.56	20.68	2.42	4.46	69.5
404 $\mu\mu$.									
Tin, pure	A	70° 33'	76° 41'	116° 53'	15.03	9.09			
	H	70° 41'	75° 29'	117° 13'	14.93	10.07			
Mean values					10.98	9.58	1.18	4.05	77.6
7 per cent. lead.	I	70° 41'	74° 58'	116° 13'	14.19	9.92	1.25	3.97	76.0
21 per cent. lead.	B	70° 33'	76° 32'	117° 42'	15.42	9.52	1.16	4.10	78.3
37.5 per cent. lead.	C	70° 33'	74° 44'	116° 42'	13.22	9.51	1.24	3.84	74.9
85.5 per cent. lead.	F	70° 36'	72° 7'	115° 30'	12.37	11.11	1.46	3.81	71.5
Pure lead.					11.17	12.11	1.63	3.73	68.5

TABLE IV.

Bismuth-mercury Alloys.

Alloy.	ϕ .	2ψ .	Δ .		$2\nu\kappa$.	ν .	κ .	Refl. Power, Per Cent.
579 μ .								
Bismuth, pure.....				9.70	19.72	2.48	3.97	64.4
Bi-Hg (40 per cent. Hg?)	70° 36'	64° 36'	124° 6'	10.32	19.11	2.38	4.00	67.7
Mercury, pure (Meier's results).....				16.7	14.2	1.62	4.39	75.3
546 μ .								
Bismuth, pure.....				9.20	18.04	2.35	3.84	63.8
Bi-Hg (40 per cent. Hg?)	70° 36'	65° 40'	122° 54'	10.92	17.91	2.24	3.99	66.1
Mercury, pure (Meier's results).....				15.2	12.3	1.48	4.17	74.9
404 μ .								
Bismuth, pure.....				7.06	11.80	1.80	3.23	60.6
Bi-Hg (40 per cent. Hg?)	70° 36'	67° 2'	110° 3'	8.33	10.44	1.59	3.29	63.6
Mercury, pure (Meier's results).....				9.2	5.8	0.92	3.17	73.3

TABLE V.

Ne²/m and W.

Bismuth-lead Alloys.										
	Per Cent. Lead.	0.	6.	19.	26.4.	48.	61.	75.	86.	100.
$Ne^2/m \times \text{const.} \dots\dots$	579 μ	131	132	134	133	137	137	137	139	143
	546 μ	133	133	132	146?	124?	137	137	137	142
	404 μ	148	147	149	141	146	144	152	147	149
$W \times \text{const.}$	579 μ	281	274	276	261	259	252	232	234	223
	546 μ	283	278	279	276	247	247	235	233	223
	404 μ	308	323	309	275	268	265	267	234	220
Cadmium-lead Alloys.										
	Per Cent. Lead.	0.	12.	22.	33.5.	52.5.	64.	76.	79.5.	100.
$Ne^2/m \times \text{const.} \dots\dots$	579 μ	92	94	101	105	112	114	122	120	140
	546 μ	93	93	103	115	114	113	122	121	141
	404 μ	95	99	115	122	123	125	129	137	149
$W \times \text{const.} \dots\dots\dots$	579 μ	52	64	97	105	123	152	186	121	223
	546 μ	51	65	100	123	137	156	184	186	223
	404 μ	46	64	92	110	140	162	214	204	229

Tin-lead Alloys.

	Per Cent. Lead.	0.	7.	21.	37.5.	62.	85.5.	100.		
$Ne^2/m \times \text{const.} \dots\dots$	$579 \mu\mu$	125	123	127	125	127	125	143		
	$546 \mu\mu$	134	127	129	125	126	124	141		
	$404 \mu\mu$	136	150	132	150	—	140	150		
$W \times \text{const.} \dots\dots\dots$	$579 \mu\mu$	114	123	126	147	173	179	223		
	$546 \mu\mu$	120	119	138	151	175	171	223		
	$404 \mu\mu$	136	150	132	150	—	182	220		

Bismuth-mercury Alloys.

	$\frac{Ne^2}{m} \times \text{const.}$			$W \times \text{const.}$		
	Bismuth.	Bi—Hg.	Mercury.	Bismuth.	Bi—Hg.	Mercury.
$579 \mu\mu \dots\dots$	131	127	92	281	257	135
$546 \mu\mu \dots\dots$	133	125	88	283	245	127
$404 \mu\mu \dots\dots$	148	129	89	308	242	123

The observational errors inherent in katoptric methods give possible variations of 3 or 4 per cent. in the values of ν and κ , and correspondingly larger variations in $\nu^2 - \kappa^2$ and $2\nu\kappa$. These limits suppose perfect metal surfaces. From an inspection of the values obtained by the writer for different surfaces of the same liquid surface it will be seen that this limit is practically attained. As observations upon different surfaces of solid metals of the same composition differ among themselves by 10 to 30 per cent. in some cases, even for the same observer, the experimental advantages of using liquid surfaces are manifest. There are no scratches or surface impurities due to abrasive material, no differential polishing of the components of an alloy, and no question of variation of surface due to heat treatment. The surfaces are always plane and can be renewed at pleasure.

The determinations made with violet light ($404 \mu\mu$) were exceedingly difficult to make on account of eye-fatigue. The values of the optical constants for this light are therefore regarded merely as a check on the other determinations.

IX. DISCUSSION OF RESULTS.

Interpretation of the above results is most conveniently made on the simple free electron theory of Drude. His conception of the free electrons ricochetting from molecule to molecule under the influence of an outside applied electromagnetic field is inadequate, especially in the light of the more recent developments of the electron theory. Nevertheless, his

classic treatment is capable of explaining and coordinating metallic phenomena qualitatively with surprising success.

Drude's¹ equations for the optical constants of the metals are as follows:

$$n^2(1 - k^2) = 1 + \Sigma \frac{\theta_h'}{1 - \left(\frac{\tau_h}{\tau}\right)^2} - 4\pi \Sigma \frac{m'N}{r^2 + \left(\frac{m'}{\tau}\right)^2}, \quad (1)$$

$$2n^2k = 4\pi\tau \Sigma \frac{Nr}{r^2 + \left(\frac{m'}{\tau}\right)^2}. \quad (2)$$

The first summation in equation (1) is a term wholly due to the molecules of the metal. The other two summations in both equations express the optical effect of the free electrons, being stated wholly in terms of their parameters and τ , the period of vibration of the light used, divided by 2π . In these latter summations, m' is equal to m/e^2 , m and e being the mass and charge of each of any group of free electrons. N is the number per cm^3 . of each group. r is equal to N/σ , σ being that portion of the total "conductivity" of the metal due to these particular electrons. σ should be equal to the electrical conductivity as usually defined for steady currents.

In this work, the following simplifying assumptions are usually made:

(a) In equation (1), the terms $1 + \Sigma \cdot \theta_h' / [1 - (\tau_h/\tau)^2]$ have been assumed to possess a value independent of the free electrons present, *i.e.*, these terms have a numerical value equal approximately to that of $n^2(1 - k^2)$ for a heavy insulator. As selective reflection is very small for the metals used in this investigation, n may be taken as about 1.6 and k as 0. Thus $n^2(1 - k^2)$ for the molecules of the metal, or its equivalent $1 + \Sigma \cdot \theta_h' / [1 - (\tau_h/\tau)^2]$ will be numerically equal to about 2.5. Since $n^2(1 - k^2)$ is a much larger negative quantity for metals, rather wide variations for this assumed value of 2.5 will not seriously affect the final results.

(b) The free electrons are assumed to be of one group, *i.e.*, they are negative electrons possessing identical mass, charge, average velocity, etc. The positive electrons are essentially molecules possessing positive charges. Being relatively large and heavy, they contribute practically nothing to the electrical and optical characteristics peculiar to metals. Their optical effect is thus entirely contained in the first summation of equation (1) given in (a).

If we divide numerators and denominators of the fractions in (1) and

¹ P. Drude, *Theory of Optics* (Mann's translation), p. 398

(2) by m'^2 and substitute m/e^2 for m' , the above equations become

$$\nu^2 - \kappa^2 = 2.5 - \frac{4\pi \frac{Ne^2}{m}}{\frac{r^2 e^4}{m^2} + \left(\frac{1}{\tau}\right)^2}, \quad (3)$$

$$2\nu\kappa = 4\pi\tau \frac{\frac{Ne^2}{m}}{\frac{r^2 e^4}{m^2} + \left(\frac{1}{\tau}\right)^2}, \quad (4)$$

where ν and κ have been used for Drude's n and $n\kappa$ respectively. r has been given as equal to N/σ . σ , the electrical conductivity, is expressible in the free electron theory of Drude by $Ne^2/m \cdot T/2$, in which T is the average value of the time between successive impacts of a free electron with successive molecules. This period is equal to the reciprocal of the number of impacts of the electron with molecules per second, and will be the same for all electrons. If we substitute $1/W$ for $T/2$, σ is equal to Ne^2/mW . W is thus a sort of quasi-frequency of impact of the free electrons. τ is now given by mW/e^2 . If this is substituted for r in equations (3) and (4), and ω for $1/\tau$ (i.e., ω for 2π times the frequency of the light used), these equations become

$$\nu^2 - \kappa^2 = 2.5 - \frac{4\pi \frac{Ne^2}{m}}{\omega^2 + W^2}, \quad (5)$$

$$2\nu\kappa = 4\pi \frac{W}{\omega} \frac{\frac{Ne^2}{m}}{\omega^2 + W^2}. \quad (6)$$

W and Ne^2/m may be computed from these equations and the values of the optical constants. The reasons for the choice of W rather than T as a free electron parameter will perhaps be evident in the discussion following.

Optical Constants in the Solid and Liquid States.—Figures 3, 4, 5 and 6 show the relations between the optical constants for the solid and liquid states of the pure metals. The data for the solid metals has been obtained from various papers. It is seen that with the exception of cadmium, these constants are roughly doubled by fusion. Figs. 7, 8 and 9 show the variation of the constants $\nu\kappa$ and $\nu^2 - \kappa^2$ for liquids, with the atomic concentration of one component. In general, these are smooth, nonlinear curves. Littleton has assumed that simple mixture in solid alloys will be shown by the straight line variation of these con-

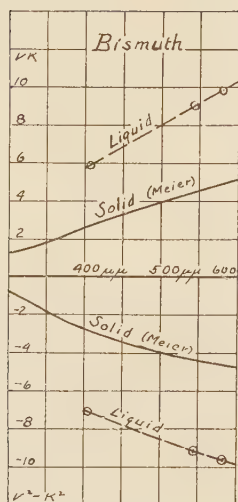


Fig. 3.

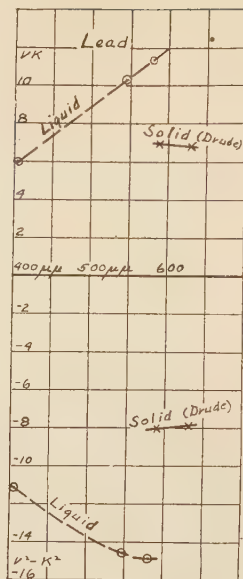


Fig. 4.

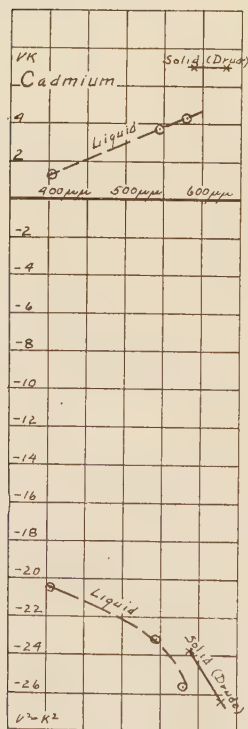


Fig. 5.

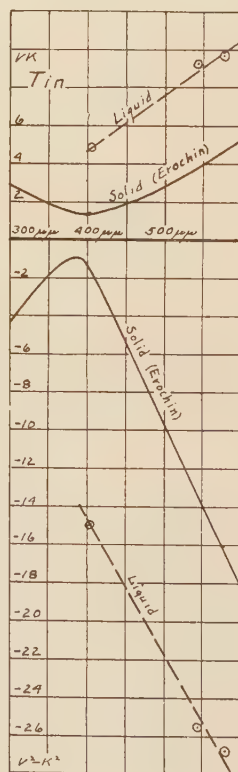


Fig. 6.

stants with the composition. This, of course, will be so where the alloy consists of two types of crystals mechanically mixed.

Theoretical Interpretation of Results.—In Table V. the calculated values of Ne^2/m and W are given for all the pure metals and alloys investigated. The units used are arbitrary. In Figs. 10, 11 and 12 they have been plotted against the atomic concentration of one component, for each series of alloys respectively.

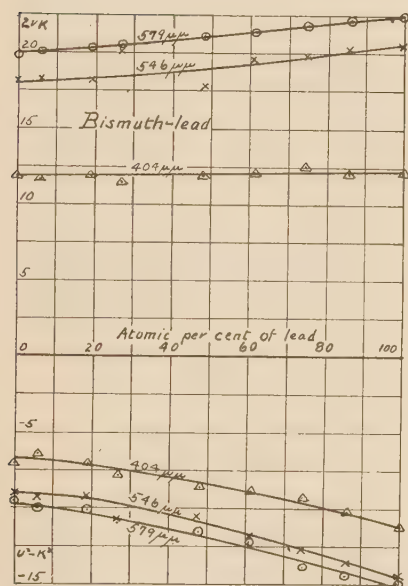


Fig. 7.

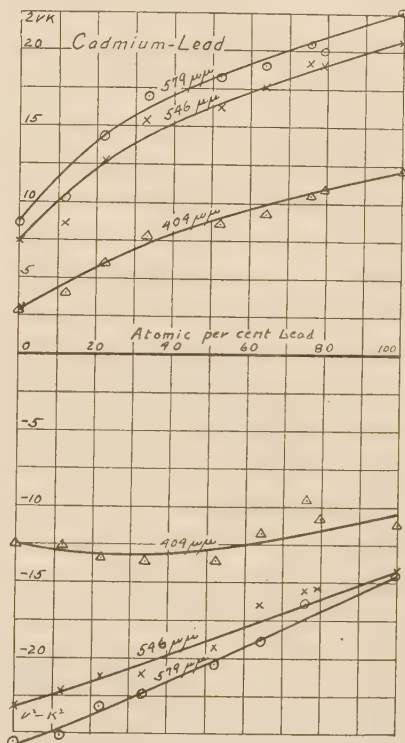


Fig. 8.

Within the limits of error, the values of Ne^2/m calculated from the optical constants for yellow and green light ($579 \mu\mu$ and $546 \mu\mu$) seem to lie on the same straight line for each series, except for the pure lead points in Figs. 11 and 12. While the results for violet light ($404 \mu\mu$) are altogether too uncertain to be used in determining any functional relationship of Ne^2/m , there seems to be no doubt that in general they lie above the other points. Ne^2/m , however, should be the same, whatever the wave-length of the light used in determining it. The discrepancy is probably due to the following causes: (a) the effect of atomic resonance may not be even approximately represented by 2.5; (b) selective reflec-

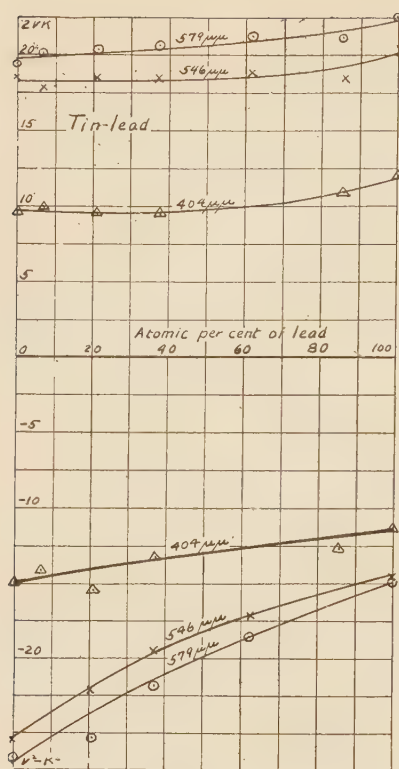


Fig. 9.

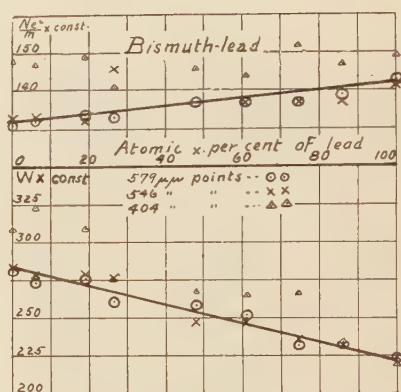


Fig. 10.

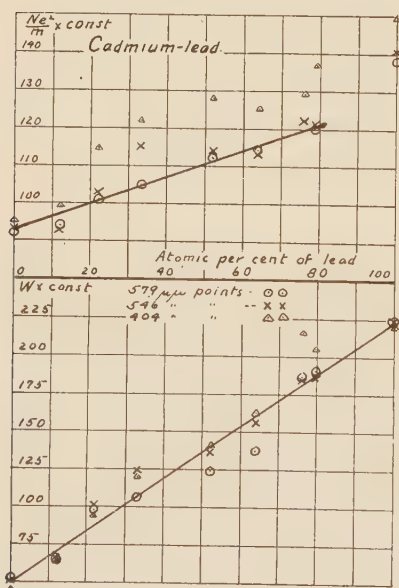


Fig. 11.

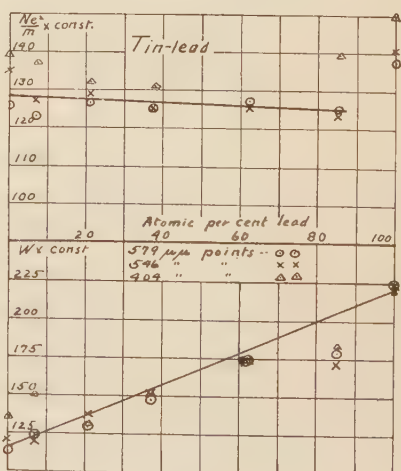


Fig. 12.

tion may be present in the ultra violet, not far beyond the visible. This is the case for most solid insulators. As selective reflection is due to the resonance of bound electrons within the atom, its presence in the atoms of most metals may be inferred. The above effect may be indicated for bismuth by the slight irregularities at the violet end of the solid curves for this metal. In the case of tin, Erochin has placed the center of an absorption band at $340\text{ }\mu\mu$. Selective reflection in the ultra-violet usually increases the value of the term in the expression of $\nu^2 - \kappa^2$ for violet light, which represents the effect of the bound electrons of the atoms, and will introduce a somewhat similar term into the expression of $2\nu\kappa$.

The probable linearity of the variation of Ne^2/m with atomic concentration is to be expected. The molecules of a liquid metal are distinct entities, practically independent of each other. The fields of force of their component electric charges are thus almost entirely internal. The conducting electrons may therefore be regarded as truly "free," and as a definite portion of the metal. Thus each component of the alloy carries to the alloy a certain number of free electrons, identical in characteristics, and the number of these in the mixture is the sum of the numbers present in each component before the alloy is formed.

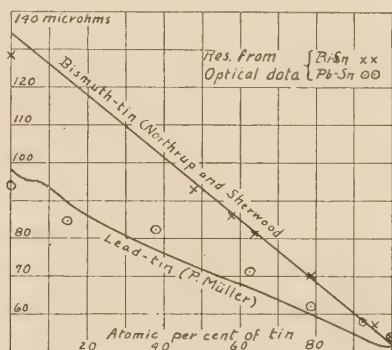


Fig. 13.

The pure lead points in the Cd-Pb and Sn-Pb figures are not collinear with the other points, and the difference can hardly be ascribed to experimental error. The cause of this variation, therefore, probably lies in some peculiarity of constitution of these alloys. Such a peculiarity is indicated by the resistances of this series of alloys, as given by P. Müller.¹ In the tin-lead series, the resistance rises uniformly with the lead content up to about 90 per cent. lead. Beyond this the resistance curve is lifted up in a small but distinct maximum (see Fig. 13). Müller gives

¹ P. Müller, *Metallurgie*, 7, 755, 1910.

the resistances of the cadmium-lead series to 6 per cent. cadmium only, but the same rise is evident. The fall of resistance from the maximum to pure lead is probably due to the anomalous increase in the number of free electrons indicated by the optical results.

In the solid state, these alloys are solid solutions at the lead side of the phase diagrams. The temperature of 400° at which the observations were made, is not far above the temperature of complete fusion, and it is quite possible that the tendency to atomic grouping shown by the solutions is carried over into the molten state. This tendency is analogous to the formation of an easily dissociated compound, and the process of grouping will result in a similar manner in the absorption of free electrons into the groups. Thus the alloy from 0 per cent. to 90 per cent. lead may be considered as a simple mixture of cadmium (or tin) and this quasi-compound, and the atomic concentration— Ne^2/m curve will be a straight line within this range. The alloy series from 90 per cent. to 100 per cent. lead should act as a mixture of the so-called compound and pure lead, in a similar manner.

Turning to the curves which show the variation of W with the atomic concentration, the agreement of the values of W given by the three lights used is very good, except for alloys rich in bismuth. The differences for this metal series may be due to either or both of the causes given for the Ne^2/m variations. It should be possible to bring the values of both Ne^2/m and W into good agreement for the three lights used, by assuming suitable values of the molecular or bound electron terms in the optical equations. However, in view of the rather large errors inherent in optical measurements on metals, it has seemed hardly worth while to do this.

The linearity of the W curves is striking, and is also a natural consequence of the liquid condition of the alloys. The frequency of impact of a free electron with the comparatively inert molecules ($2W$) is proportional to the "total surface of impact" of the molecules. If we introduce into the assemblage of like molecules of the one metal molecules of another metal which are of a different size, the "total surface of impact," and therefore the frequency of impact of a free electron, are both obviously linear functions of the atomic concentration of either component.

It should be noticed that there is no indication in these curves of any peculiarity of cadmium-lead and tin-lead alloys rich in lead, such as that shown by the variation of Ne^2/m . The tendency towards atomic grouping which would account for this variation cannot be very great. This is shown in P. Müller's work. As the temperature is increased the irregularities of the concentration-resistance curves of these alloys dis-

appear. Owing to this looseness of grouping there is no marked shielding of one atom by another. This will be especially true if the targets of impact are the atomic nuclei. Under these conditions the frequency of impact of any free electron will be unaffected by such tendencies, and the variation of W with atomic concentration will be linear. If true compounds were formed, however, the close association of atoms might be expected to influence this free electron parameter.

Thus the variation of the free electron functions, Ne^2/m and W in these binary alloys and the coherence of results, seem to confirm very strongly the admissibility of the application of the simple form of the electron theory to liquid metals. However, any satisfactory optical theory should be able to show a quantitative relation between the electrical and optical characteristics of metals. Any of these characteristics or any of the parameters of the conducting electrons, should be determinable from a sufficient number of the remainder. For instance, Drude,¹ Schuster,² W. Meier³ and others have calculated the number of free electrons per atom in various solid metals from the optical constants and electrical conductivity. Rubens and Hagen⁴ tested the relationship of the electrical conductivity and reflecting power of metals given in the equation $1 - R = 2/\sqrt{\sigma T}$, in which R is the reflecting power, σ the electrical conductivity and T the frequency of the light used. This equation is not valid for visible light but holds very well for the infra-red (25.5μ) with one or two exceptions. These exceptions have been held to be due to the neglect of "resonance of the molecules" in the electromagnetic theory of Maxwell, from which the equation is derived. Now Drude's equations, forms of which are used in this paper, are recognized as a better representation of the optical behavior of metals, than Maxwell's original equations. $1 - R = 2/\sqrt{\sigma T}$ may be derived from Drude's equations if we assume W very large in comparison with ω , *i.e.*, that the time between successive impacts of an electron may be neglected in comparison with the period of the light used in the optical determinations. Thus the lack of agreement of Maxwell's equation with facts in the case of bismuth and one or two other metals is probably due to the omission of a term which has nothing to do with "resonance of the molecules."

In general it may be said that when solid metals are used, the data obtained from electrical measurements agree rather poorly with those from optical measurements in the visible spectrum. This may be illus-

¹ P. Drude, *Ann. d. Phys.*, 14, 936, 1904.

² A. Schuster, *Phil. Mag.*, 7, 151, 1904.

³ W. Meier, *Ann. d. Phys.*, 31, 1016, 1910.

⁴ Rubens and Hagen, *Ann. d. Phys.*, 11, 873, 1903.

trated very well for the solid state of the metals which were investigated in this work. From equations (5) and (6) we may obtain

$$\frac{Ne^2}{m} = -\frac{\omega^2}{4\pi} \frac{(\nu^2 - \kappa^2 - 2.5)^2 - (2\nu\kappa)^2}{(\nu^2 - \kappa^2 - 2.5)}$$

and

$$W = -\frac{\omega 2\nu\kappa}{(\nu^2 - \kappa^2 - 2.5)}.$$

The electrical restivity (in electrostatic units) is Wm/Ne^2 and substituting from the equations above,

$$\text{Res. (e.s.u.)} = \frac{4\pi}{\omega} \frac{2\nu\kappa}{(\nu^2 - \kappa^2 - 2.5)^2 - (2\nu\kappa)^2}.$$

I have used the data of the various writers from which the solid metal curves of Figs. 1, 2, 3 and 4 were drawn to calculate the restivities. These are expressed in microhms and compared with the electrical resistivities of the same solid metals as given by the Smithsonian Tables, as follows:

	Bismuth.	Lead.	Cadmium.	Tin.
Light used.....	600 $\mu\mu$	600 $\mu\mu$	560 $\mu\mu$	550 $\mu\mu$
Res. (microhms) by opt. methods....	238	159	58	76
Res. (microhms) by Smiths. Tables....	119	22	7.5	14

The lack of agreement indicated above has been explained on the supposition that the resistivity at frequencies approaching that of light is markedly different from that at ordinary frequencies. Livens¹ and others have developed this functional relation. Owing to the simple conditions existing in molten metals, it should be possible to use their optical constants to gain considerable information as to this possible variation of resistivity, and as to the identity of the electrical and optical parameters given in the elementary equations. On this account I have calculated the resistivities of the pure molten metals from the optical data I have obtained. These and various electron parameters are given in the following table. Only the optical results for yellow and green light were used, those for violet light having altogether too large experimental errors. Meier's² results were used for mercury. The resistivities so obtained, are compared with those found by Northrup and Suydam³ for bismuth, lead, cadmium and tin at 400°. While no particular effort

¹ G. H. Livens, *Phil. Mag.*, 30, 112, 1915.

² W. Meier, *loc. cit.*

³ E. F. Northrup and V. A. Suydam, *Journ. Franklin Inst.*, 175, 153, 1913.

was made to keep the temperature of the liquid metals constant during the optical investigation, it was never very far from this value. The resistivity of mercury at ordinary temperatures was used.

TABLE VI.

	Bismuth.	Lead.	Cad- mium.	Tin.	Mercury (Meier).
$Ne^2/m \times 10^{-28}/9$	132	142.5	92.5	129.5	90
N (No. free electrons per cm. ³) $\times 10^{-22}$	14.7	15.9	10.3	14.5	10.0
No. atoms per cm. ² $\times 10^{-22}$	2.9	3.1	4.3	3.5	4.1
No. free electrons per atom	5.1	5.1	2.4	4.1	2.5
$W \times 10^{-12}/6\pi$	282	223	51.2	117	131
Impacts of free electron per sec. $(2W) \times 10^{-14}$	106	84	19.5	44	50
Impacts per period of green light $(550 \mu\mu)$..	19.3	15.3	3.5	8.9	9.0
Wm/Ne^2 (resistivity, e.s.u.) $\times 6.60 \times 10^{-7}$..	2.14	1.57	0.56	0.90	1.46
Resistivity in microhms from above data ..	128	94	33.4	54	87.3
Resistivity in microhms from electrical data ..	134	98	34	52	94
Ratio "optical" to electrical resistivity	.95	.96	.98	1.04	.93

An auxiliary figure (Fig. 13) is also given which compares the resistivities of tin-lead and tin-bismuth alloys, electrically and optically determined. The electrical data for the two series of alloys are taken from papers by P. Müller,¹ and by E. F. Northrup and R. G. Sherwood² respectively. The "optical" resistances of the tin-lead alloys were taken directly from the optical results of this series. As the optical characteristics of tin-bismuth alloys were not investigated, the "optical" resistances of this series were calculated from the electron parameters Ne^2/m and W of the pure metal. Both of these are linear functions of the atomic concentration, provided that no compounds are present in the liquid state, and may be easily determined for an alloy of the two metals of any given atomic composition. The quotient of these two will give the resistivity.

From an inspection of the tables and auxiliary figures, it may be seen that, except for mercury, the electrically and optically determined resistivities agree, in every case, within the limits set by unavoidable experimental error. The optical constants of mercury were not determined by the writer and their accuracy is not known, although it is probably good. There is no evidence of any change in the electrical resistivity, even up to the frequencies of light. Certainly any such variation is not greater than 5 per cent. The agreement of the results, both electrical and optical is a strong confirmation of the existence of essentially "free" electrons in these liquid metals. In view of the

¹ P. Müller, *loc. cit.*² E. F. Northrup and R. G. Sherwood, *Journ. Franklin Inst.*, 182, 477, 1916.

probable validity of this conception, I have calculated the values of N , the number of free electrons per cm.³, the number per atom, the frequency of impact of the free electrons ($2W$) and the ratio of this frequency to that of green light ($550\ \mu\mu$). The number of free electrons per atom necessitated a knowledge of the number of atoms per cm.³ For each metal this number is equal to Avogadro's number multiplied by the density and divided by the atomic weight. Avogadro's number was taken as 60×10^{22} . The densities of the molten metals are not accurate, as the temperatures at which they were taken were not given in the tables consulted. To calculate the number of electrons per cm.³, e was taken as equal to 4.77×10^{-10} e.s.u. and m to 9×10^{-28} g. It is evident that the uncertainties of the various constants used in these calculations render the values of the number of free electrons per atom only approximations at best. In addition it is probable that the parameters Ne^2/m and W given here, in reality include constant multipliers. These would be introduced in a more exact development of the free electron theory.

From certain points of view it would seem that the number of free electrons per atom, or at least per molecule, should be an integer for each metal. The accuracy of the present work is not sufficient to settle this point. On the other hand, the uncertainties of the constants used to obtain these relations, affect all alike, and it is possible to obtain these ratios as integers, within the limits of experimental error, by making small and legitimate changes in the above doubtful constants. The results are certainly not inconsistent with the possibility of these integral relations.

From the agreement of the electrical and optical data in Table VI., it seems that changes of resistivity at light frequencies, and molecular resonance (except in infrequent cases) are negligible factors in determining the phenomena of these liquid metals. I can see no reason why they should be of any greater importance in solid metals, and the discrepancies encountered in the explanation of the optical and electrical phenomena of the solid phase must be due to some different cause. The distinguishing characteristic of the solid metal is the space lattice structure of its crystals. This structure demands that the atoms should have strong external fields of force, binding them into a rigid form. The conducting electrons can hardly wander freely in inter-atomic space, between so-called impacts. From various points of view it is hard to avoid the conclusion that conduction in crystalline solids is due to the "handing along" of these electrons from atom to atom. Thus, in the fundamental equations of motion of a conducting electron in the metallic crystal, a term must be present which is a function of the position of the electron within

the space lattice. It is probable that the neglect of such a term is the source of apparently discordant electrical and optical results for solid metals.

The small range of temperature and the limited accuracy of the experimental work made impossible the detection of measurement of any temperature effect on the optical constants. Such measurement would be of value from a theoretical standpoint.

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